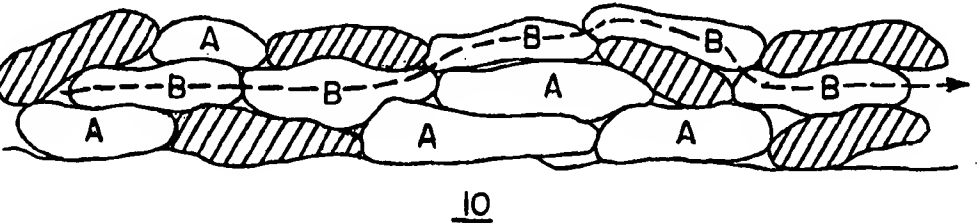




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> :  <b>H05B 3/26, 3/14, F27D 11/02</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 98/51127</b></p> <p>(43) International Publication Date: <b>12 November 1998 (12.11.98)</b></p>
<p>(21) International Application Number: <b>PCT/US98/09261</b></p> <p>(22) International Filing Date: <b>6 May 1998 (06.05.98)</b></p> <p>(30) Priority Data:  <b>60/045,907</b>      <b>6 May 1997 (06.05.97)</b>      <b>US</b></p> <p>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application  <b>US</b>      <b>60/045,907 (CIP)</b>  Filed on      <b>6 May 1997 (06.05.97)</b></p> <p>(71) Applicant (for all designated States except US): <b>THERMOCE-  RAMIX, L.L.C. [US/US]; 101 Federal Street, Boston, MA  02110 (US).</b></p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): <b>ABBOTT, Richard, C.  [US/US]; 68 Old Colonial Drive, Gardner, MA 01440 (US).  MAGNANT, Gary, P. [US/US]; 49 Pigeon Hill Street,  Rockport, MA 01966 (US). COREY, George [US/US]; 65  Harding Street, Newton, MA 02165 (US). SANDUEN, Ole  [US/US]; 20-2 Federal Street, Salem, MA 01970 (US).</b></p>	<p>(74) Agents: <b>HOOVER, Thomas, O. et al.; Hamilton, Brook, Smith  &amp; Reynolds, P.C., Two Militia Drive, Lexington, MA 02173  (US).</b></p> <p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR,  BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,  GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ,  LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW,  MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO  patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian  patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR,  IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF,  CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b>  <i>With international search report.</i></p>	
<p>(54) Title: <b>DEPOSITED RESISTIVE COATINGS</b></p>		
		
<p>(57) Abstract</p> <p>The present invention involves coatings deposited on a substrate including a layer having a selected resistivity. The resistive layer can serve as a heat source in a variety of applications and can be fabricated using an arc plasma spraying procedure.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

-1-

## DEPOSITED RESISTIVE COATINGS

## RELATED APPLICATION(S)

This application claims the benefit of U.S. Provisional Application Serial No. 60/045,907 filed on May 6, 1997 and relates to U.S. Serial No. \_\_\_\_\_ being filed simultaneously herewith, and the above applications being incorporated herein by reference.

## BACKGROUND OF THE INVENTION

Arc plasma spraying is a method for depositing materials on various substrates. A DC electric arc creates an ionized gas (a plasma) which is used to literally spray molten powdered materials in a manner similar to spraying paint. It was first developed by the aerospace industry where a need existed for different high performance coatings that afforded better thermal protection, electrical insulation and mechanical wear resistance. The technology has since found many applications in other industries because the coatings are typically of high density, good adhesion, and relatively low cost. One of the major advantages of the method is that it is amenable to volume manufacturing. For example, plasma sprays have been used to manufacture millions of alternator parts per year with aluminum oxide.

Plasma spray is part of a larger class of technology called, thermal spray, which includes combustion and

-2-

electronic arc methods for depositing metal and ceramic coatings.

A thermal sprayed coating has a unique microstructure. During the deposition process, each particle enters a gas stream, melts, and cools to the solid form independent of other particles. When molten particles impact the substrate being coated, they impact ("splat") as flattened circular platelets and freeze at high cooling rates. The coating is built up on the substrate by traversing the gun apparatus repeatedly over the substrate building up layer by layer until the desired thickness of coating has been achieved. Because the particles solidify as splats, the resultant microstructure is very lamellar with the grains approximating circular platelets randomly stacked above the plane of the substrate.

A continuing need exists for improvements, however, for improved materials in many fields using thermal spraying.

#### SUMMARY OF THE INVENTION

The present invention relates to the fabrication and use of resistive heaters with a controlled resistance such that when a voltage is applied to the material, heat is generated.

A heater of this invention includes a resistive heating layer including an electrically-insulating composition mixed with an electrically-conducting composition and a third composition. The electrically-conducting composition has a higher electrical resistance than the electrically-conducting composition.

In a preferred embodiment, the resistive heating layer has the distinctive microstructure of a thermal-sprayed coating and is electrically coupled to a voltage source. In a further preferred embodiment, the resistive heating

-3-

layer further includes a third material including an additive that enhances a material property of the resistive heating layer. In another preferred embodiment, the substrate, the electrically-insulating composition and the electrically-conducting composition are ceramic. In yet another preferred embodiment, the third material includes a conductive material or a thermal conductor. In other preferred embodiments, the heater includes a nozzle or a tubular body that heats material within the body.

10 In a method of this invention, an electrically-conducting composition with an electrically-insulating composition and a third material to form a mixture. The mixture is then thermal sprayed onto a substrate, and a heater is formed with the sprayed mixture.

15 In a preferred embodiment of this method, a bonding layer is formed between the substrate and the heater. In another preferred embodiment the substrate is removed from the thermal sprayed mixture. In yet another preferred embodiment, the third material includes a second electrical insulating layer. Still another preferred embodiment includes the formation of a heat reflecting layer. In a further preferred embodiment, a rapid thermal heater for a semiconductor processing system is formed. Additionally, a resistive heating layer is preferably formed that includes silicon carbide, molybdenum disilicide, lanthanum chromate, zirconium diboride or titanium diboride. In the thermal spraying step, a plurality of layers are preferably sprayed.

30 Another embodiment of this invention is a plasma-sprayed resistive heater including a resistive heating layer including a first electrically-insulating material mixed with a second electrically-conducting material which has a lower electrical resistance than the electrically-insulating material and further mixed with a third

-4-

material. A voltage source is electrically coupled to the resistive heating layer. Preferably, the electrically-insulating material and the electrically conducting material are both ceramic.

5       A rapid thermal processor of this invention includes an enclosure which defines a reaction chamber. A support structure for mounting an article to be processed is mounted within the reaction chamber, and a heater module which includes a resistive heating material is mounted  
10       within the reaction chamber.

Another rapid thermal processing apparatus of this invention includes an enclosure which defines a reaction chamber, a support structure for mounting an article to be processed, a heater module, and electrical contacts. The  
15       support structure is mounted within the reaction chamber. The heater module is also within the reaction chamber and includes silicon carbide. An electrical current flows through the silicon carbide to heat the article.

Advantages of embodiments of this invention that have  
20       a resistive heating layer include the capability of quickly cycling between processing temperatures due to the extremely low mass of the resistive heating layer. Further, the design of the heater module affords extensive flexibility in heater configuration allowing the heater to  
25       be easily designed to include multiple zones of the resistive heating layer that can be independently powered to compensate for unequal heat losses between the center and edge of an article to be heated. Enhanced control over the composition of the resistive heating layer, in  
30       accordance with this invention, further provides greater latitude in heater design and greater control over the amount of heat generated.

-5-

## BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following, more particular description of preferred  
5 embodiments of the invention, as illustrated in the accompanying figures. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

Figure 1a is an illustration of deposited  
10 microstructure of this invention

Figure 1b is a graphical illustration of resistivity as a function of coating composition.

Figure 2 illustrates a layered structure including an electrically resistive layer that was plasma sprayed onto a  
15 substrate in accordance with the invention.

Figure 3 is a cross-sectional view of an embodiment of this invention, wherein a resistive heating layer using lengthwise conduction is formed between insulating layers on a conductive substrate.

20 Figure 4a is a cross-sectional view of a rapid thermal processing apparatus of this invention.

Figure 4b is a cross-sectional view of a second embodiment of a rapid thermal processing apparatus of this invention.

25 Figure 5 is an illustration of a silicon carbide resistive heater of this invention.

Figure 6 is a magnified view of offset cuts in the silicon carbide heater shown in Figure 5.

Figure 7 is a cross-sectional side view of a depressed  
30 wafer bed in the silicon carbide heater.

Figure 8 is a cross-sectional view of a sparkless ignition device in accordance with the invention.

-6-

Figure 9a is an interior cross-sectional view of a chemically-resistant thermally-sprayed heater pipe for low to high temperature applications.

Figure 9b is a perspective side view of the heater pipe shown in Figure 9a.

Figures 10a-10b include an interior cross-sectional view and a cross-sectional side view of a low-temperature heater on a metal or plastic pipe.

Figure 11 is an impeller made in accordance with the invention.

Figure 12 illustrates a method of making a heated nozzle having a high abrasion resistance.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The features and other details of the method of the invention will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. Numbers that appear in more than one figure represent the same item. It will be understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of this invention can be employed in various embodiments without departing from the scope of the invention.

Resistive heating compositions can be deposited by arc plasma spray. When the compositions are to serve as a coating, the coatings typically have high bond strength with the substrate, ranging up to 10,000 psi in tension (normal to the plane of the coating) with shear strengths (parallel to the plane of the coating) four to eight times higher. Such strong adhesion often allows materials with dissimilar thermal expansion coefficients to reach elevated temperatures without delamination due to thermoelastic stresses. In addition, the intimate contact between

**SUBSTITUTE SHEET (RULE 26)**



-7-

coating and substrate permits excellent heat transfer across the coating/substrate interface. Preferably, the thermal spraying is performed in a vacuum to reduce surface defects in the sprayed coating.

5 A coating, in the form of a resistive heating layer of this invention, comprises at least one material, preferably a low-density ceramic that possesses the following qualities: an ability to withstand high temperatures, a resistance to oxidation, and a low mass for rapid  
10 temperature response to voltage inputs. The resistive heating layer is also highly refractory so that a fairly high power density is achievable.

A variety of carbides, borides, silicides, and oxides have electroconducting properties that are appropriate for  
15 use in this invention. In a preferred embodiment, the resistive heating layer is formed of either silicon carbide (SiC) or molybdenum disilicide (MoSi<sub>2</sub>). Other suitable materials from which the resistive heating layer can be formed include lanthanum chromate, zirconium diboride  
20 (ZrB<sub>2</sub>) and titanium diboride (TiB<sub>2</sub>).

In another preferred embodiment, the resistive heating layer is composed of a mixture of at least two materials, one material being electroconductive (low resistivity) and the other material being insulating (high resistivity).  
25 The overall resistivity of the resistive heating layer is controlled by blending the materials prior to deposition in such proportions that, when they are deposited as a coating by, for example, arc plasma spraying, the desired resistivity is obtained.

30 The starting materials for forming the resistive heating layer can be mixed using one of several different techniques. For example, the materials can be mechanically blended, where the materials are mixed using conventional blending techniques. Another option is to use binders,

-8-

where the powders are mixed with liquid binders, such as polyvinyl alcohol or polystyrene. The powders are then dried, crushed and sieved. The resultant powder contains the binder which burns off during the thermal spray  
5 process. A third option is spray drying, where the materials are mixed in a fine powder form with some liquid, usually water, then sprayed through a nozzle to form spherical agglomerates, which, on average, consist of particles having the desired composition.

10 If the starting powder consists of a blend of two or more different materials, the plasma sprayed coating microstructure will be a lamellar array of two or more kinds of grains. As shown in Figure 1a, the two different materials can be viewed as forming two interpenetrating,  
15 interconnected lattices with the degree of interconnection being a function of the proportion of material that is present. In particular, if one material happens to be electrically insulating, and one electrically conducting, then the conductivity (or resistivity) will depend upon the  
20 degree of interconnectedness of the conducting material. In Figure 1a, the deposited microstructure includes 3 discrete phases of different materials deposited on a substrate 10. Materials A and B are insulator and conductor, respectively. The cross-hatched phase is added  
25 for modified engineering properties, such as hardness, thermal emissivity, or thermal expansion. The dashed line indicates electric current path through the lattice.

A general representation of the relationship between the balance of powder composition and resistivity is  
30 illustrated in Figure 1b. The powder comprises an electroconducting material (represented on the left side of the graph as 0% insulator concentration) and an insulating material (represented on the right side of the graph as 100% insulator composition). The horizontal axis indicates

-9-

the fraction of insulator blended into the composite. As is evident from the chart in Figure 1b, a mixture of powders that has a high proportion of low resistivity material will have, when deposited as a coating by plasma spray, a low resistivity. Similarly, the same two materials blended with a large proportion of high resistivity material will have a correspondingly high resistivity as a plasma-sprayed coating.

For a deposited coating to use a desired power level to generate a particular amount of heat when a voltage is applied, the coating generally must have a particular resistance that is determined by the desired power level. The resistance,  $R$ , is calculated from the applied voltage,  $V$ , and the desired power level,  $P$ , as follows:

$$R = V^2/P$$

The resistance of the coating is a function of the geometry of the coating. Specifically, the resistance of the coating can be measured in terms of the electric current path length ( $L$ ) the cross sectional area ( $A$ ) through which the current passes, and the material resistivity ( $\rho$ ) by the following equation:

$$R = \rho \cdot L / A$$

Therefore, to design a coating for a given power level and a given geometry that will operate at a given voltage, one has only to determine the resistivity of the material using the following equation:

$$\rho = R \cdot A / L = V^2 \cdot A / (P \cdot L)$$

-10-

A composition with the necessary resistivity,  $\rho$ , as determined, above, can be found empirically using varying blends of conductors and insulators.

The fact that the resistivity is a controlled variable is significant because it represents an additional degree of freedom for the heater designer that ordinarily does not exist. In most existing situations, the resistivity of the heater material, e.g., nichrome, is a fixed value, forcing the designer to develop a heater geometry, by manipulating L and A, to obtain the desired power.

For example, if it is desired to heat a tube by winding nichrome wire around it, the designer must choose the correct diameter wire for A, the cross sectional area through which the electric current must pass, and the spacing of the windings for L, the total path length of the electric current.

It is often problematic achieving this balance of  $\rho$ , L, and A simply because of the commercial availability of the desired wire size. If a coating is to be used, the L and A parameters are simply determined by the dimensions of the tube and the coating thickness. There is no limitation in  $\rho$  because that can be formulated in the starting powders.

The starting materials cover a very wide range of chemical compositions. This disclosure focuses on ceramics for the low resistivity material because in general they can withstand high temperatures, frequently possess good oxidation resistance, and often have low mass for rapid temperature response to voltage inputs. In addition, they have, in general, a good coefficient of thermal expansion match with the insulating component. Such electroconducting materials include carbides such as silicon carbide or boron carbide, borides, silicides such as molybdenum disilicide or tungsten disilicide, and oxides

-11-

such as lanthanum chromate or tin oxide which have electroconducting properties that are appropriate for the technology. For the insulating material, oxides are very good in the application, particularly  $\text{Al}_2\text{O}_3$ , which is refractory, insulating, and inexpensive. Aluminum nitride and mullite are also suitable as insulating ceramics

In a preferred embodiment, the resistive heating layer is a mixture of materials with positive and negative coefficients of resistivity which can cross compensate for each other over a range of temperatures. Examples of such mixtures include molybdenum disilicide ( $\text{MoSi}_2$ ) and lanthanum chromate ( $\text{LaCrO}_3$ ), where the resistivity of molybdenum disilicide will increase with temperature, and the resistivity of lanthanum chromate will decrease with temperature such that a combination of the two can provide fairly constant resistance over a range of temperatures. Another example of such a mixture includes titanium diboride ( $\text{TiB}_2$ ) and silicon carbide ( $\text{SiC}$ ).

In another preferred embodiment, resistive heaters, heated parts and resistive coatings comprise three or more materials (e.g., ceramics, metals, polymers, glasses, cermets), at least two of which are ceramics, formed by thermal spray processes to enhance desirable engineering properties, including the following: thermal conductivity, resistivity range, emissivity, bonding, hardness, ductility, thermal expansion compatibility, porosity, chemical resistance (especially oxidation resistance, reduction resistance, or molten metal resistance), negative temperature coefficients (NTC) and positive temperature coefficients (PTC), self-regulating heating systems, decorative finish applications, catalytic properties, sintering, reflective properties, sensing capabilities, and filtering properties. All thermal spray processes can be used to make multi-phase resistive heaters.

-12-

For example, in a resistive coating including molybdenum disilicide and mullite, any of a variety of additives can be supplied to enhance various properties. Aluminum nitride, for example, is added to enhance thermal conductivity and temperature uniformity, and it is particularly useful in applications involving thermal cyclers or constrained geometries. Lanthanum chromate is added to expand the range of achievable resistivities of the coating and allows more precise determination of desired power density. Aluminum oxide is added to increase heater emissivity and is particularly useful in radiant heaters. Molybdenum is added to increase bonding of the resistive heating layer to the metallic or ceramic substrate. Silica or metals are added to modify the ductility, substrate compatability, interparticle cohesion and coefficient of thermal expansion (CTE) through low elastic modulus. Polystyrene is added and is oxidized to leave a porous heater structure particularly suitable for filters or membranes. Glass formers (e.g., silica), oxides, and precious metals are added for oxidation resistance. Platinum is added for catalytic conversion of hydrocarbons at elevated temperatures. Finally, silicon carbide or silicon nitride is added to modify resistivity.

In a resistive heating layer of titanium diboride and aluminum oxide, for example, other additives are also employed. For example, yttrium oxide is added as a sintering aid to densify a spray-formed nozzle/heater. Magnesium zirconate is added for molten metal resistance and is particularly useful in aluminum processing applications. Chromium-doped aluminum oxide (synthetic ruby) is added to provide color to the heater. Further, aluminum nitride is added to increase thermal conductivity.

In yet another example, in a resistive heating layer including zirconium diboride and aluminum oxide, chromium

-13-

boride is added to increase the hardness and abrasion resistance of the heater and is particularly useful in the pumping of petroleum crude oil and abrasive slurries.

Moreover, materials which ordinarily can not be thermally-sprayed, such as silicon carbide, aluminum nitride, and silicon nitride can be deposited with carrier materials that melt. Further, structural enhancements to heater coatings or free standing parts can be accomplished by injecting ceramic fibers, for example, into the plasma stream. Winding filaments during heater deposition can also add strength.

The electrically resistive ceramic coatings can be configured in a variety of ways, depending on the application. In general, the path of conduction can be either through the thickness of the coating or through the length of the coating. If it is through the thickness of the coating, usually the ceramic is sprayed directly on the substrate or on a substrate which has been previously sprayed with a bond coat. Then a metal contact layer can be deposited on the top surface of the ceramic layer. An example of a multilayer structure 11 is illustrated in Figure 2. In this structure a bonding layer 14 such as a nickel-aluminum alloy is formed on a substrate 12 such as a metal or carbon fiber element. Note that the surface of the substrate 12 can also be roughened, by grit blasting for example, to provide better adherence. Next an electrically insulating layer 16 such as aluminum oxide is formed. This is followed by the electrically resistive ceramic layer 18 sandwiched between electrical contact layers 17 and 19. Next, a second electrical insulating layer 20, which can also be a ceramic, is applied. A thermally insulating ceramic coating 24 such as zirconium dioxide is then applied. Emissive coatings, such as

-14-

chromium oxide, can replace layers 20 and 24 in an alternative embodiment.

If electrical conduction is through the length of the coating, as in Figure 3, then an insulating layer 16, such as aluminum oxide, can be deposited over the substrate 12 and bond coat 14 if the substrate 12 is a conductor so as to prevent shorting to the substrate 12. Likewise, a second insulating layer 20, preferably another ceramic, can be deposited on top of the resistive heating layer 18 to electrically isolate the resistive heating layer 18. Contact pads 17 and 19 provide lengthwise conduction through the resistive heating layer 18.

In another embodiment, the resistive heating layer 18, is deposited in a nonuniform pattern on the substrate 12. In a further preferred embodiment, the pattern includes a resistive heating layer 18 in the form of a discrete and independently powered regions. These regions can be formed, for example, by deposition or spraying on a masked substrate. The independently-powered regions enable the heater to achieve precise temperature control and uniform temperatures across the wafer, thereby reducing thermal stress in the wafer. In one embodiment, the resistive heating layer 18 is denser or more highly concentrated at positions proximate to the edge of the wafer to provide more heat at the edges of the wafer to counteract the more rapid rate of heat loss that occurs at the edge of the wafer in comparison to the center of the wafer.

In other embodiments, the heater module also includes at least one other layer such as a conducting film, an additional resistive film, or a layer that can reflect or emit heat from the heater module in a selected pattern. One or more layers can also be included to provide improved thermal matching between components to prevent bending or fracture of adjacent layers having different coefficients



-15-

of thermal expansion. In another preferred embodiment, a very rough surface is applied to the outer surface of the heater to improve heat transfer to the (nitrogen) gas media. The bond layer may be graduated in composition for  
5 a better match in coefficients of thermal expansion.

Other plasma-sprayed coatings may be deposited to effect different engineering purposes. For example, thermal barrier coatings such as  $ZrO_2$  to thermally insulate the heater from either the top or bottom, or high thermal  
10 emissivity coatings such as  $Cr_2O_3$  for efficient radiant heat transfer.

The composition of the outermost deposited surface of the heater is preferably selected according to the method of heater transfer being utilized. If the heat transfer to  
15 the wafer is principally radiative, then its outermost surface preferably comprises a material with high thermal emissivity. On the other hand, if heat is being transferred mainly by conduction, then a highly conductive surface is preferred. When heat is transferred by  
20 convection, the desired material is one whose heat transfer coefficient is most compatible with the gaseous medium.

A rapid thermal processing system of this invention that uses one or more ceramic resistive heaters for the processing of semiconductor wafers is illustrated in Figure  
25 4a. An enclosure 30 defines a chamber for RTP. A semiconductor wafer 32 is supported by pins 40 upon a support plated 38 mounted on a pedestal 36, and is placed near or in direct contact with a ceramic heater 34. The wafer 32 can be raised, lowered, or rotated (to prevent  
30 more uniform heating) within the chamber by means of a drive mechanism connected with the pedestal 36. The support plate 38 is a round plate constructed of an insulating material, such as quartz or various other ceramics and it reflects much of the radiation emitted from

-16-

the heated wafer 32. Three pins 40 are mounted on top face of the support plate 38. The pins are preferably formed of quartz, as well, and are pointed at their top ends to establish minimal contact with the wafer 32 which rests upon these pointed ends.

A second heater 42 is provided at the bottom of the chamber and is used for preheating a wafer 32 before processing by heater 34. In other embodiments, however, either heater 34 or 42 can be used to process the wafer 32. The wafer 32 is moved from heater 34 to heater 42 by the drive mechanism raising the pedestal 36. Thermocouples 44 are embedded within small-diameter wells in each of the heaters 34 and 42 to measure the temperature of the heaters. The temperature of the wafer 32 will approximate the temperature of a heater with which it is in close proximity or in contact.

In one embodiment, each heater is a multilayer ceramic device, such as those illustrated in Figures 2 and 3, with a resistive heating layer spray-coated on a thermally insulating substrate (e.g., aluminum oxide). Preferably, the thickness of the resistive heating layer is less than 0.25 inches. Each of the heaters 34, 42 are driven by a voltage source electrically coupled with the resistive heating layer. When the voltage source applies a voltage to the resistive heating layer, heat is generated. Optionally, additional layers are coated on the resistive heating layer in order, for example, to prevent a wafer from being contaminated by the heater or its substrate, to prevent adhesion of the wafer to the heater, or to create an emissive surface for a radiative ceramic heater.

In an alternative embodiment, illustrated in Figure 4b, heater 42 includes at least 3 bores which allow passage of support pins 40 extending all the way from the wafer 32, through the heater 42 and out of the chamber. In this

-17-

embodiment, the pins 40 can be jointly raised or lowered to change the position of the wafer 32 in the chamber.

In another alternative embodiment, the heaters 34, 42 are formed of silicon carbide, preferably in monolithic  
5 form. A silicon carbide heater of this invention is illustrated in Figures 5-7. As shown in Figure 5, the silicon carbide heater is in the form of a square plate 90. In one embodiment, the square plate has a thickness of 3 mm and a length and width of 10 inches. The square plate 90  
10 is enclosed in a fused silica frame 94. The frame 94 supplies the plate 90 with greater strength.

A series of cuts 92 are machined into the square plate 90 alternating from opposite sides of the plate 90. The cuts 92 create a winding path through which current must  
15 flow to traverse the square plate 90, and are illustrated in a side view in Figure 6. The cuts 92 are machined into both of the planar faces of the square plate 90 in an offset pattern. Use of an offset pattern reduces radiant heat loss through the heater.

20 In the illustrated embodiment, a half-millimeter depression 96 is machined into a planar face of the square plate 90 to hold a semiconductor wafer. The machined depression 96 is shown, from a cross-sectional side view, in Figure 7. On the face of the plate 90 opposite the  
25 depression, a half-millimeter protrusion is machined to maintain a constant thickness across the plate 90. Within the depression 96, three or more small through-bores are cut to allow fused silica wafer-support pins to pass.

Additional bores are cut into the plate 90 at opposite  
30 corners. Electrical connectors 98, 100 are made of SiC graphite (a special grade of graphite with a thermal expansion coefficient approximately equal to silicon carbide) and are coated with chemically vapor deposited silicon carbide. As shown, these connectors 98, 100 are

-18-

mounted within the bores. The electrical connectors 98, 100 are sized with a cross-section that will generate a resistance at the applied voltage, wherein the resistance will generate heat at a rate which will offset heat loss from the plate 90 through the electrical connectors 98, 100. As a result, the electrical connectors 98, 100 will provide neither a substantial net supply nor loss of heat, and, accordingly, will not substantially affect the temperature of the plate.

10        Bores are also cut into the frame 94 at the two corners which are unsupported by electrical connectors, and fused silica legs 102, 104 are mounted within these bores to provide added, and more balanced support, for the heater.

15        Processing steps for which the RTP system of this invention is suitable include resident reactions such as annealing, sintering, silicidation, and glass reflow. The apparatus and methods can also be used to promote surface interactions between the substrate and reactive gases, for example, oxidation and nitridation of the article being processed. Further still, the apparatus and methods of this invention can be used for epitaxial reactions, wherein a material, such as silicon, is deposited in monocrystalline form on a heated substrate. Finally, the apparatus and methods can also be used for chemical vapor deposition, wherein the product of reactant gases is deposited on a heated substrate in noncrystalline form.

Examples of other plasma-sprayed heater applications are as follows:

30        1. Titanium boride/aluminum oxide blanket heater on pipe with metal contact layer on top and aluminum oxide insulator on the contact.

-19-

2. Silicon carbide/aluminum oxide heater tip for natural gas ignitor on kitchen stove, oven, water heater or heating system.

3. Free standing molybdenum disilicide/mullite muffle tube fabricated by sprayforming on a removable mandrel.

4. Low voltage zirconium diboride/aluminum oxide heater coating.

5. Laboratory Applications: Resistively heated ceramic coated lab vessels; work trays; tubing; piping; heat exchangers; heatable filters; frits; incubators; benchtop heaters; flameless torches; waterbaths; drybaths; heat platens; reaction vessels; reaction chambers; combustion chambers; heatable mixers and impellers; heating electrodes.

6. Industrial applications: Sparkless ignition systems; bar heaters; strip heaters; combustion chambers; reaction chambers; nozzles and pipes; static and active mixers; chemical processing equipment and machines; room heaters; heated impellers and mixing tanks.

7. Home and office applications: Ignitors; grills; heated mixers; impellers; and stirrers.

8. Complex aluminum oxide; ceramic and or metal parts. Plasma sprayed heaters of unusual geometry; variable resistivity heaters allow more heat to be placed in certain heater locations and less heat in other locations; whole surface geometric heaters; direct contact heaters; pure ceramic heating systems; ceramic coated metal heating systems; use of masks to plasma spray heater coating of defined geometry; and pre-heaters to warm surfaces.

Illustrated in Figure 8 is a sparkless ignition device including a housing 52 having positive and negative contacts, an insulator coating 54 and a resistive coating 56 on a distal end that is heated to ignite a liquid or gas exposed to the thermal emission.

-20-

Figures 9a and 9b illustrate a chemically resistant, thermally-sprayed heater pipe for low to high temperature applications. A removable mandrel 110, preferably, of graphite, serves as a base for a sequence of coatings.

5 First, aluminum oxide is arc plasma sprayed onto the mandrel 110 to form an electrically insulating and chemically resistive layer 111. Next, a resistive-heating layer 112 is sprayed onto the aluminum oxide layer 111. The resistive-heating layer 112 can be in the form of a

10 patterned element. An outer aluminum oxide layer 113 is then applied to provide an insulating and chemically-resistant outer barrier. The end of the pipe is masked during the spraying of layer 113, and electrical contacts 114 are then applied to the resistive heating layer 112.

15 The electrical contacts are of a conductive ceramic, metal or composite material and can be applied by sputtering, spraying or mechanical methods. The mandrel is removed by heating it until it is freed by shrinkage or is burned off.

Figure 10 illustrates a low-temperature heater on a

20 metal or plastic pipe. If the pipe 120 is metal, a layer 121 of insulating material is applied. If the pipe 120 is plastic, a layer 121 of bond coat is applied. Next, a resistive heating layer 122 is applied, followed by an insulating layer 123, which is preferably a polymeric

25 coating. Again, the resistive heating layer 122 is masked at its end when the insulating layer 123 is applied. Electrical contacts 124 are then applied to the resistive heating layer 122 where it was masked. Finally, current leads 124 are attached to the electrical contacts 125.

30 In Figure 11, an impellor 60 is shown with a shaft end 62 that connects to a motor to provide rotation. The shaft 64 has electrical contacts and the impellor element 66 can be a metal base having an insulator, a ceramic resistive coating, sprayed copper contacts and an outer insulation

-21-

layer. This structure is rapidly heatable, chemically resistant, temperature resistant up in 1200°C in air or up to 2000°C in selected atmospheres.

Shown in Figure 12 is a method 80 of fabricating an electrically resistive high temperature nozzle. A removable mandrel 82 is provided with a mask 84. The coating 86 as described above is applied and the masks and mandrel are removed at 88. The device can include built-in thermocouples, electrical contacts and connectors for attachment to a fluid supply.

While this invention has been particularly shown and described with references to preferred embodiments thereof, those skilled in the art will understand that various changes in form and details may be made therein without departing from the scope of the invention as defined by the appended claims.

-22-

## CLAIMS

The invention claimed is:

1. A thermally sprayed heater comprising:  
a resistive heating layer including a first  
5 electrically-insulating material mixed with a second  
electrically-conducting material, the electrically-  
insulating material having a higher electrical  
resistance than the electrically-conducting material.
2. The heater of Claim 1 wherein the resistive heating  
10 layer has the microstructure of a thermal-sprayed  
coating.
3. The heater of Claim 1 further comprising a voltage  
source electrically coupled to the resistive heating  
layer.
- 15 4. The heater of Claim 1 wherein the resistive heating  
layer further includes a third composition of an  
additive that enhances a material property of the  
resistive heating layer.
5. The heater of Claim 1 wherein the heating layer is on  
20 a substrate comprising a ceramic material.
6. The heater of Claim 1 wherein the electrically-  
insulating composition and the electrically-conducting  
composition are ceramic.

**SUBSTITUTE SHEET (RULE 26)**



-23-

7. A method for making a heater comprising the steps of:  
mixing an electrically-conducting material with  
an electrically-insulating material; and  
thermal spraying the electrically-conducting  
material and the electrically-insulating material to  
form a heater.
8. The method of Claim 7 further comprising mixing a  
third material with the conducting and insulating  
materials.
9. The method of Claim 7 wherein the conducting and  
insulating materials comprise ceramic.
10. The method of Claim 7 further comprising connecting a  
voltage source to the thermally sprayed material.
11. The method of Claim 7 wherein the thermal spraying  
step comprises plasma spraying a plurality of layers  
on a substrate.
12. The method of Claim 7 further comprising forming a  
thermal reflector with the heater.
13. A rapid thermal processing apparatus comprising:  
an enclosure defining a reaction chamber;  
a support structure mounted within the reaction  
chamber, the support structure mounting an article to  
be processed within the reaction chamber; and  
a heater module mounted within the reaction  
chamber, the heater module including a resistive  
heating material.

-24-

14. The rapid thermal processing apparatus of Claim 13 wherein the resistive heating material includes an electrically-insulating composition mixed with an electrically-conducting composition, the electrically-insulating composition having a higher electrical resistance than the electrically-conducting composition.
15. The rapid thermal processing apparatus of Claim 13 wherein the resistive heating layer includes a composition selected from the group consisting of carbides, borides, silicides, and oxides.
16. The rapid thermal processing apparatus of Claim 13 wherein the resistive heating layer includes a composition selected from the group consisting of silicon carbide, molybdenum disilicide, lanthanum chromate, zirconium diboride, and titanium diboride.
17. The rapid thermal processing apparatus of Claim 13 further comprising a voltage source electrically coupled with the resistive heating material.
18. The rapid thermal processing apparatus of Claim 13 wherein the resistive heating material forms a pattern of independently powered regions on a substrate.
19. The rapid thermal processing apparatus of Claim 13 wherein the heater module can make direct contact with a wafer mounted on the support structure.
20. The rapid thermal processing apparatus of Claim 13 wherein the resistive heating material is a plasma sprayed lamellar structure on a substrate.

SUBSTITUTE SHEET (RULE 26)

-25-

21. The rapid thermal processing apparatus of Claim 13 wherein the resistive heating material comprises silicon carbide.
22. A method for heating a semiconductor wafer comprising  
5 the steps of:  
    positioning the wafer relative to a heater module having a resistive heating layer on a substrate to heat the wafer; and  
    applying a voltage to the resistive heating layer  
10 to generate heat in the resistive heating layer and heat the wafer.
23. A rapid thermal processing apparatus comprising:  
    an enclosure defining a reaction chamber;  
    a support structure mounted within the reaction  
15 chamber, wherein the support structure is suitable for mounting an article to be processed within the reaction chamber;  
    a heater module mounted within the reaction  
    chamber, wherein the heater module includes silicon  
20 carbide; and  
    electrical contacts in contact with the silicon carbide, such that an electrical current flows through the silicon carbide to heat the article.
24. The rapid thermal processing apparatus of Claim 23  
25 wherein the heater consists of a monolithic silicon carbide heating plate.

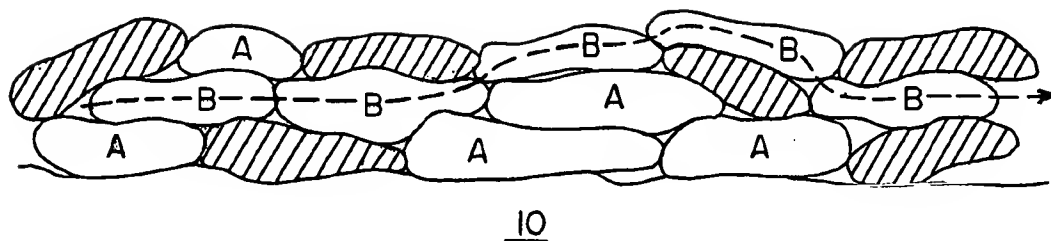


FIGURE 1A

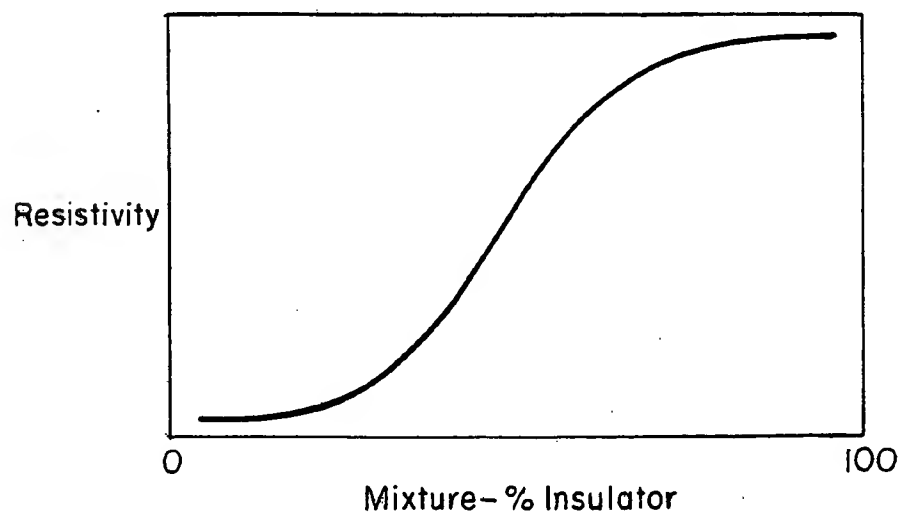


FIGURE 1B

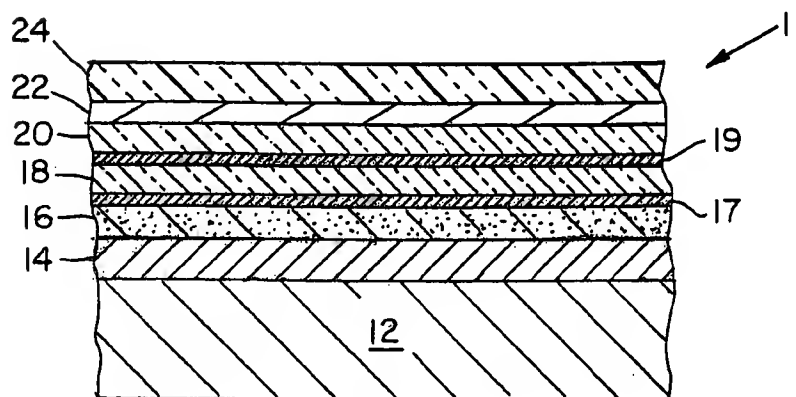


FIGURE 2

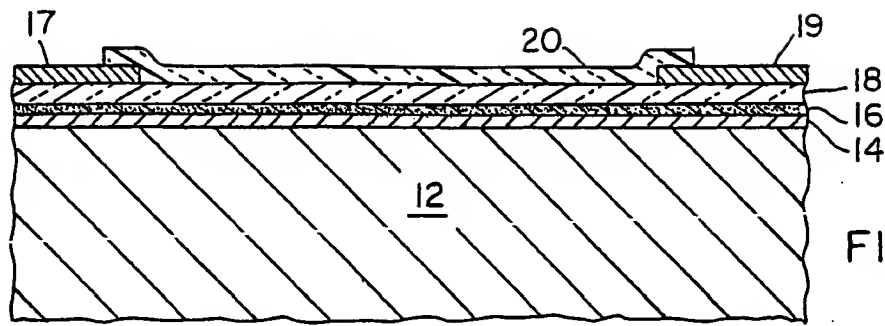


FIGURE 3

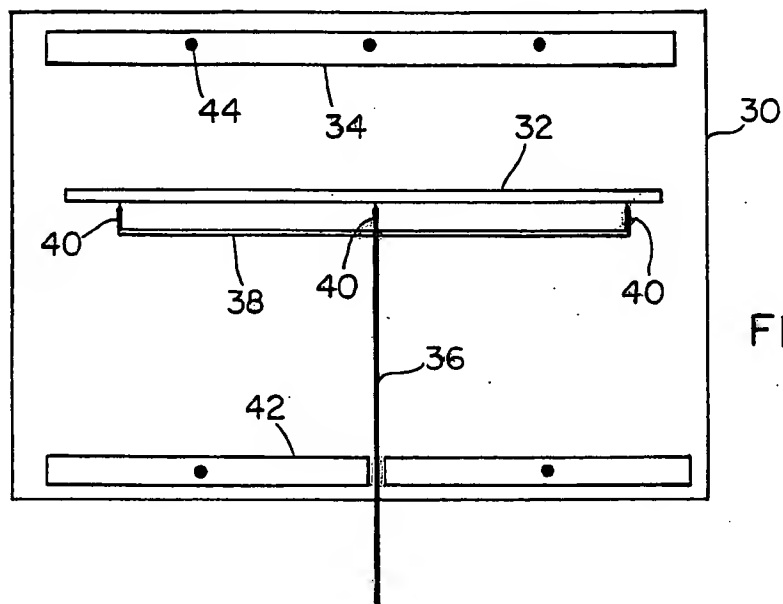


FIGURE 4A

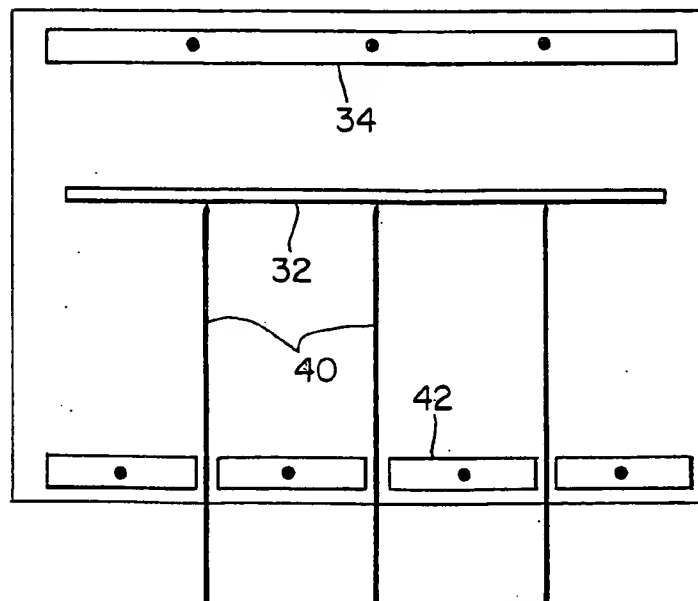


FIGURE 4B

SUBSTITUTE SHEET (RULE 26)

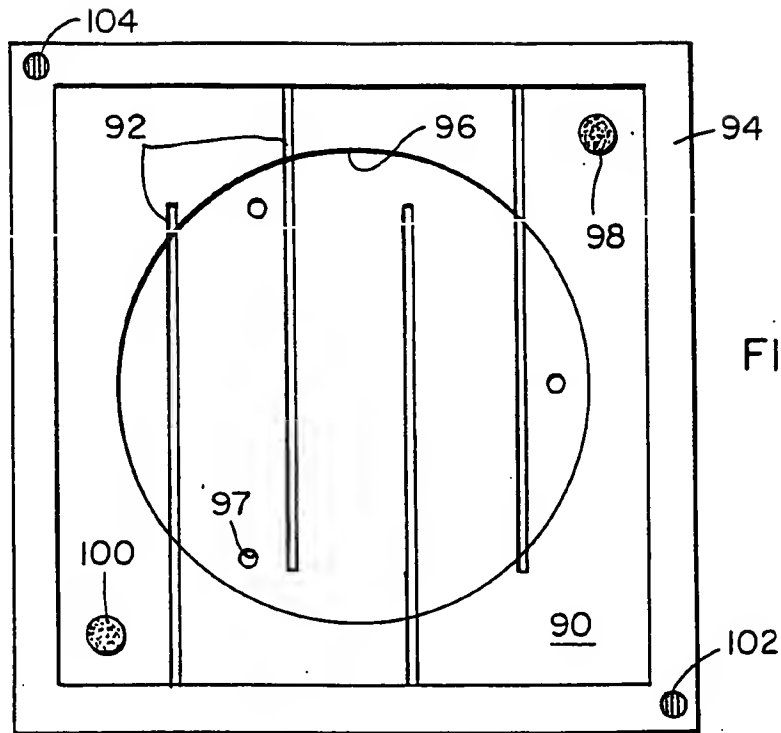


FIGURE 5

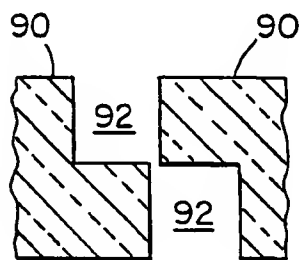


FIGURE 6

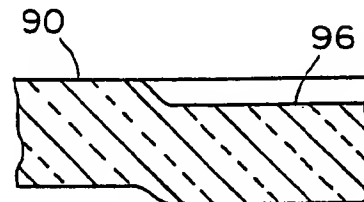


FIGURE 7

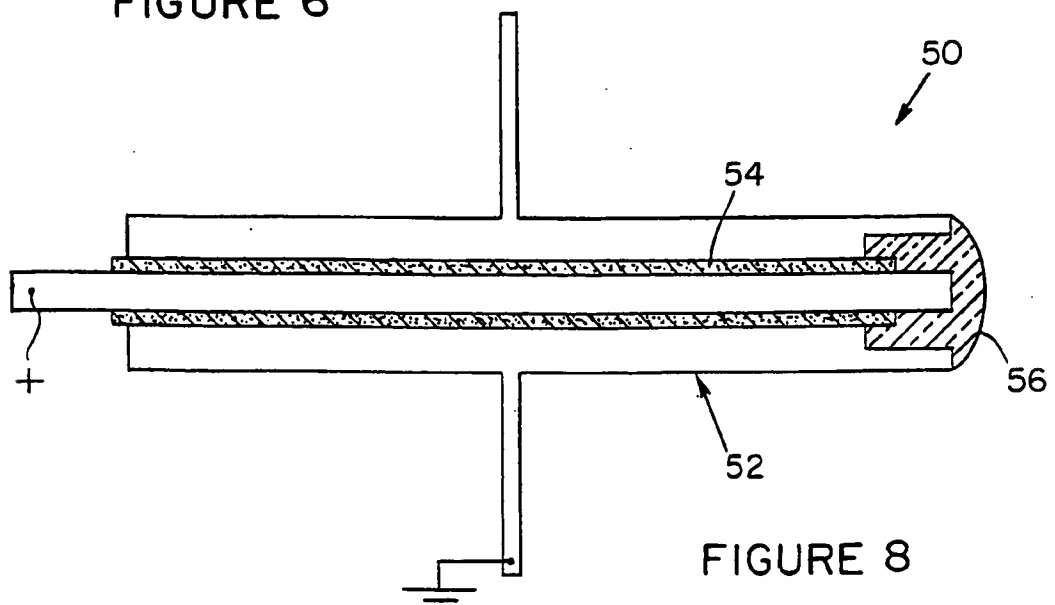


FIGURE 8

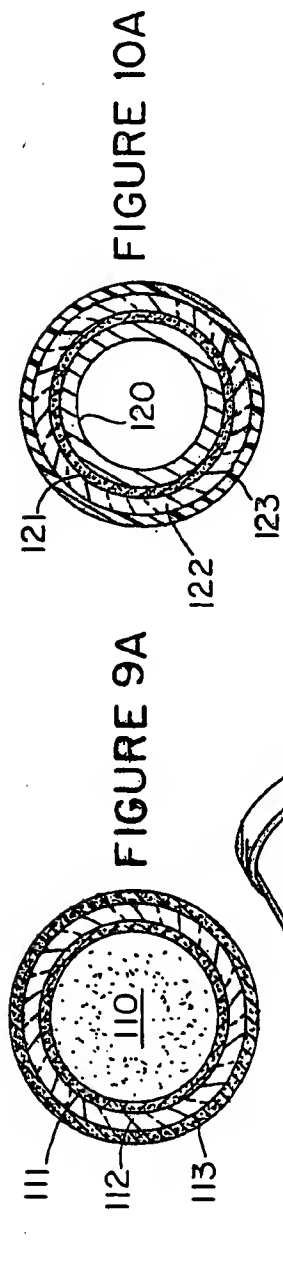


FIGURE 10A

FIGURE 9A

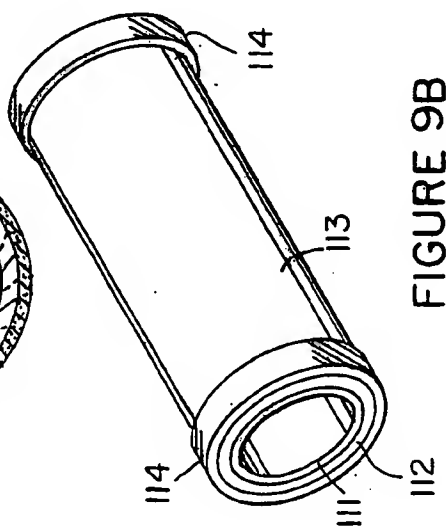


FIGURE 9B

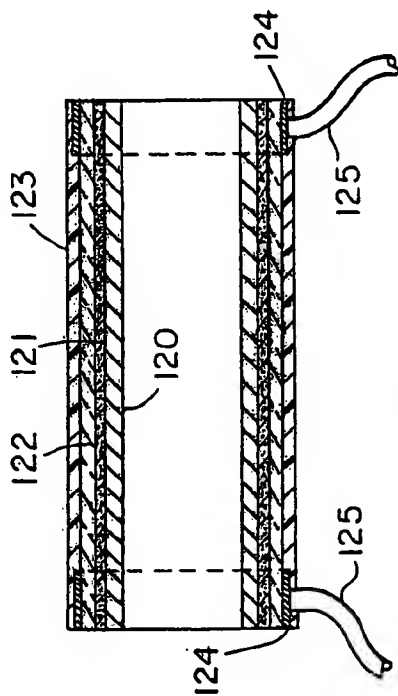


FIGURE 10B

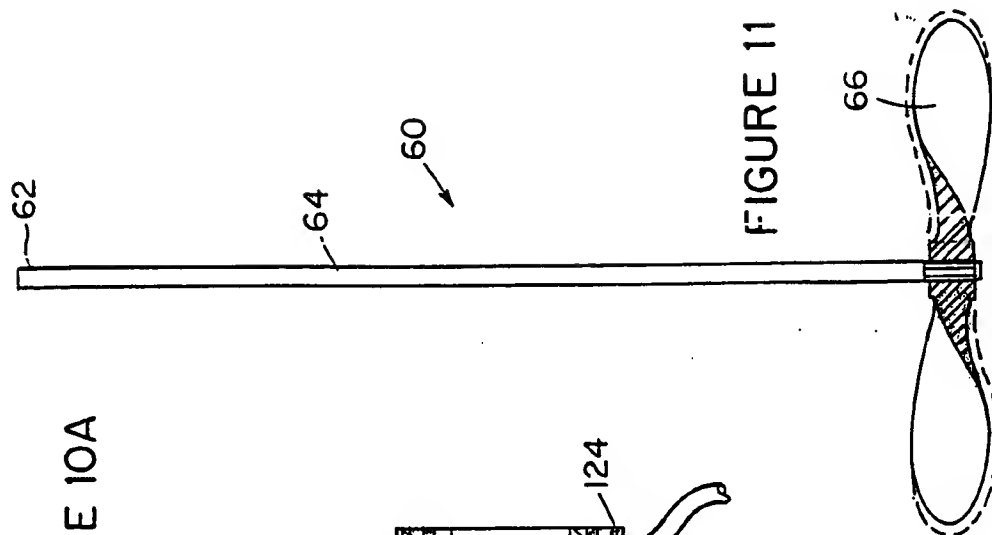


FIGURE 11

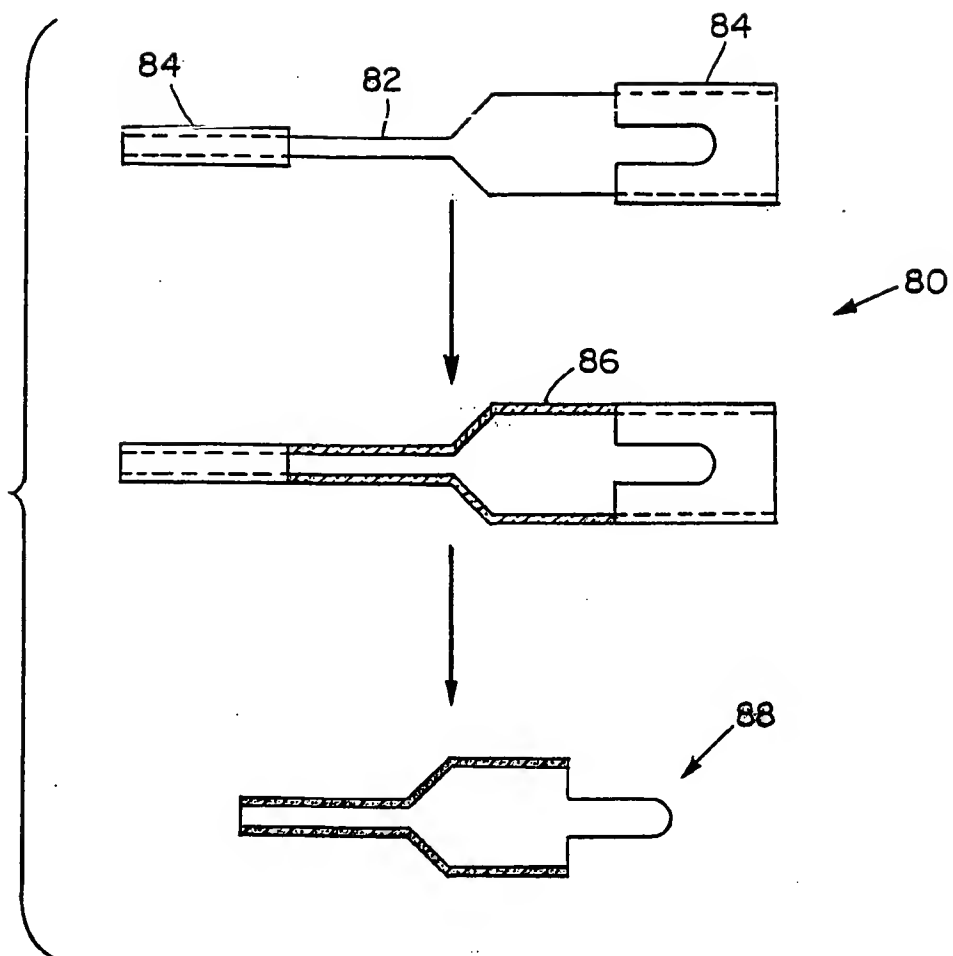


FIGURE 12



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/09261

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H05B3/26 H05B3/14 F27D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H05B F27D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 099 670 A (SMITHS INDUSTRIES PLC) 8 December 1982 see claims 1-14	1-11, 13-17
X	DE 33 25 204 A (REIMBOLD & STRICK) 24 January 1985 see claims 1-8, 14	1-11, 13-17
X	V.H.PITT: "THE PENGUIN DICTIONARY OF PHYSICS", PENGUIN BOOKS LTD., HARMONDSWORTH, MIDDLESEX, ENGLAND XP002073977 see page 194, right-hand column, paragraph 6	1
A	US 3 425 864 A (MOREY GLEN H) 4 February 1969 see claim 1	1, 11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 August 1998

Date of mailing of the international search report

25/08/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 apo nl,  
Fax: (+31-70) 340-3016

Authorized officer

De Smet, F

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/09261

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category <sup>2</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 924 497 A (AKTIEBOLAGET KANTHAL) 24 Apr11 1963 -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/09261

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2099670 A	08-12-1982	NONE	
DE 3325204 A	24-01-1985	NONE	
US 3425864 A	04-02-1969	NONE	
GB 924497 A		NONE	